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STABILITY OF SOME CENTRES IN QUARTZ

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Abstract—Electron spin resonance (ESR) is a promising dating method for Quaternary sediments. A preliminary ESR analysis was done on quartz grains extracted from sediments baked by lava-flows of Massif Central (France). For this type of sample, zeroing occurs during heating. To test the reliability of the method, the palaeodoses were determined from centres (Al and Ti) and compared with those obtained by the thermoluminescence (TL) method.

The annealing temperature and sunlight have an effect upon the stability and the behaviour of the different ESR signals. An attempt to correlate ESR signals and the red TL peak is made in terms of the variation of these two factors.

INTRODUCTION

QUARTZ is a mineral with a stable structure which is well defined, so, we can use the electron spin resonance (ESR) method. ESR lines are generally narrow, allowing accurate measurements of g-values. The main centres known in quartz are aluminium, titanium, germanium, E' and oxygen centres.

Our quartz samples were extracted from sediments baked by lava-flow which originated from the Tartaret volcano at Neschers (Massif Central, Chaîne des Puys, France) and are called C94. For these samples, zeroing was made by heating, and hence there is no problem. Previous studies have been carried out, particularly on Al and Ti centres (Yokoyama *et al.*, 1985a).

Thermoluminescence (TL) studies have also been done on the C94 samples (Sanzelle *et al.*, 1984).

In the present work, we searched for possible correlation between TL peaks (and especially the red peak at 380°C, which is the best-behaved) and ESR signals. In order to perform these experiments, light exposure and thermal annealing were used.

EXPERIMENTAL

The C94 samples were collected by D. Miallier. Locally, the lava-flow thickness is around 6–8 m and the sample was extracted from about 10 cm below the sediment–lava interface. So it was expected that the sediment was originally annealed around 800°C, with a very slow cooling rate. The method used for the sample preparation was that used by TL investigators, and was done under subdued light. This procedure has been described previously (Yokoyama *et al.*, 1985a, b). Then, in order to protect the samples from light exposure, they were enclosed in light-tight bags.

Aliquots of about 300 mg of 100–200 μm separated quartz were irradiated with a ^{137}Cs gamma source (delivering 3.8 10^{-2} Gy s^{-1}). Afterwards, the samples were split into two series, one for TL and the other for ESR studies.

The measurements were carried out with an ESR spectrometer Varian E109 with a microwave frequency of 9 GHz (X band). The hyperfine structure of signals Al and Ti may be disturbed if there is too much dipolar magnetic interaction created by the vicinity of nuclear spins. These conditions can be decreased by working at a low cavity temperature. In addition, Al and Ti centres are not superposed, which allows for a comparative study. The ESR thermal annealing treatments were done in an automatic regulating furnace ($\pm$1°C of accuracy).

For TL studies, experiments were made at a heating rate of 5°C s^{-1} in flowing nitrogen. The TL equipment was built in the Clermont laboratory, using Georges Valladas plans as concerns hardware (unpublished). The PM tube was a bi-alkali EMI 9635 QA.

ESR CENTRES

E′ *centre*

This is one of the most studied centres in quartz. It has been well characterized in alpha quartz and silica glass (Griscom, 1978). Its g-value is 2.0005. The intensity of the E' centre of quartz extracted from quaternary sediments often decreases after ^{60}Co gamma-ray irradiations, in regard to that of natural samples. This indicates that the E' centre is already saturated in these non-irradiated samples (Yokoyama *et al.*, 1985b). We did not see the E' centre in our Neschers samples.

Oxygen centre

The oxygen-associated hole centres are not well characterized in alpha quartz. Two types of OH centres have been proposed in silica glass (Stapelbroek and Griscom, 1978). One of them has been found in igneous, sedimentary and metamorphic quartz. McMorris (1970) attributed this signal to centres in amorphous, glass-like regions of structural damage created by nuclei recoiling in alpha-emission, and he called this centre the radiation damage centre. It was later found to be a peroxyradical (Griscom and Friebele, 1981). We did not observe this damage centre in our C94 samples.

In Fig. 1, we can observe an "unidentified" signal at $g = 2.01$, which is close to the g-value of the non-bonding oxygen hole centre ($g_2 = 2.0095$). The intensity of this signal is very small in the most irradiated sample. The growth curve was determined only to study the thermal stability of this centre.

Germanium centre

This type of centre is well known in alpha quartz and many studies carried out on germanium ions substitutional at Si sites. Its g-value is 1.996. Weil (1984) described the structure of this centre.

For our samples, this signal becomes detectable only after gamma-ray irradiations. The same phenomenon was observed for two palaeolithic sunlight bleached sediments (Yokoyama *et al.*, 1985b). McMorris (1971) also reported the absence of Ge signal in his natural samples. He explained it by the natural optical bleaching or by the natural change of the alkali ion states associated with the Ge centre. For our samples, the possibility of a natural optical bleaching may be excluded. Therefore, the second explanation of McMorris may be suitable. On the other hand, Shimokawa *et al.* (1984) used the Ge centre signal for the ESR dating of quartz in a volcanic rock. The Ge centre was also observed in natural quartz extracted from mylonite (Fukuchi, 1988). Therefore, the vanishing (or the persistence) of the Ge centre signal depends on the nature of rock, and cannot be generalized. Figure 1 shows a Ge centre signal in one of our irradiated samples.

Titanium centre

Some electron traps exist in natural quartz and are attributed to substitutional Ti (Weil, 1984). In addition to hyperfine structure (*hfs*) due to major Ti isotopes, the signal exhibits alkali superhyperfine structure (*shfs*). The Ti centre has three main components at $g = 1.910$, $g = 1.930$ and $g = 1.980$. The signal height is measured from the top alkali *shfs* ($g = 1.930$) to the bottom of it, as indicated by the arrows (Fig. 2).

Aluminium centre

The Al centre is a hole centre. In quartz there is a substitution of Si by Al plus one interstitial cation which maintains charge neutrality (Weil, 1984). The Al centre is characterized by a *hfs*. This centre has

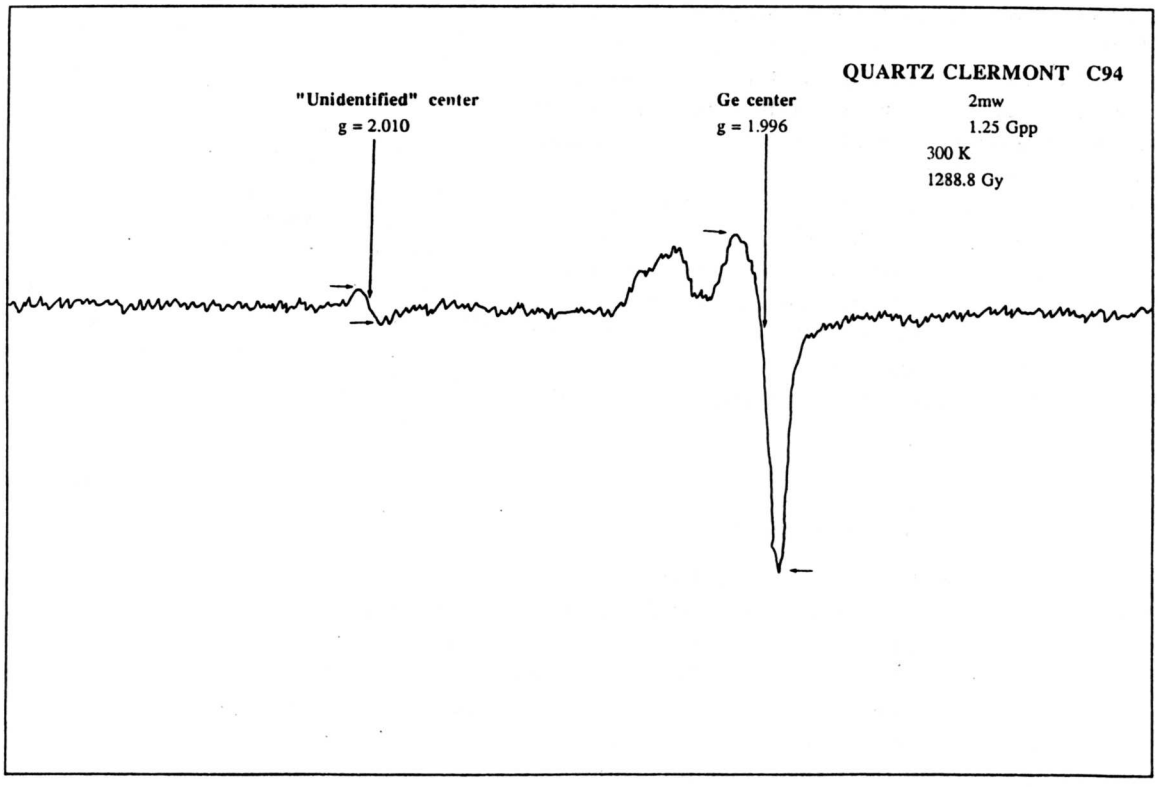

FIG. 1. ESR spectrum of OH and Ge centres of an irradiated quartz sample (C94). These centres are observed at a cavity temperature of 293 K. A microwave power of 2 mW is used. The arrows indicate how the signals' heights are measured.

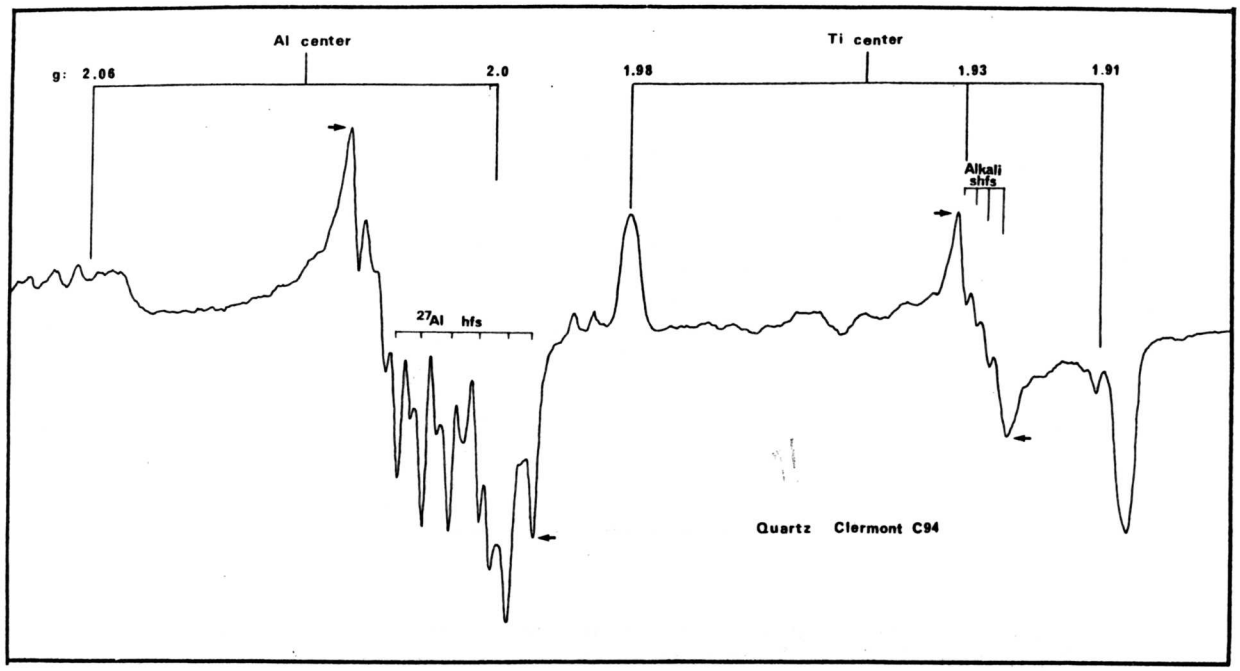

FIG. 2. ESR spectrum of Al and Ti centres of quartz from Neschers sediment (C94). ESR cavity temperature of 93 K is used. The microwave power is 5 mW for Al centre and 20 mW for Ti centre.

two main components at $g = 2.010$ and $g = 2.060$. The black arrows in Fig. 2 show how the signal height was measured.

TL SPECTRA

The natural TL signal (NTL) exhibited three peaks (Fig. 3) which can be characterized by their temperature on the glow curve and also by their colour (Miallier *et al.*, 1990). A minor peak lies around 400 nm at 220°C; the main peak is visible in a wide region of the spectrum, at least between 300 and 550 nm, and rises at 320°C, and a red peak (RTL) around 600–620 nm rises at 380°C. After gamma-irradiation in the laboratory these peaks grow, and others, which probably are not stable at room temperature, appear (Fig 4).

ESR–TL COMPARISON

Palaeodoses and ages

As shown in Table 1, the palaeodoses obtained by the ESR method (Al and Ti centres) are poorly consistent with those obtained by TL method (additive technique). For TL, the palaeodose was derived from extrapolation using the growth curve obtained with an annealed and re-irradiated sample ("second growth"), and there is great confidence in the result (Pilleyre *et al.*, 1990).

The ESR palaeodoses were determined by the additive method and obtained by using a saturating exponential fit, because no "second growth" was measured. In TL, from several experiments, we know that growth curves cannot be entirely fit by a saturating exponential fit, and the discrepancy increases as the dose increases. This can explain why, although they nearly merge at low doses, the two ESR (Al and Ti) growth curves do not give equal palaeodoses when they are exponentially fit. The Ti signal exhibits a saturating exponential-like growth, slightly above

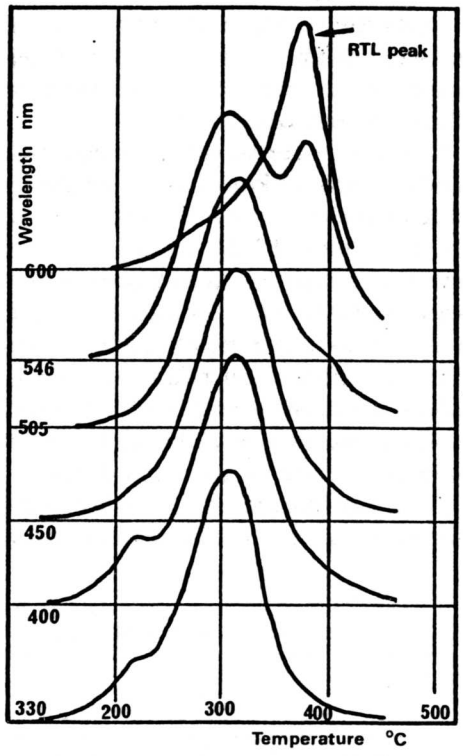

FIG. 3. Natural glow curve of C94 quartz sample (palaeodose about 70 Gy) as seen through various narrow band interferential filters. The curves are normalized and the blackbody background was subtracted. Atmosphere: nitrogen; heating rate: 5°C s^{-1}. The peak observed here around 600 nm is typical of the so-called RTL (from Miallier *et al.*, 1990).

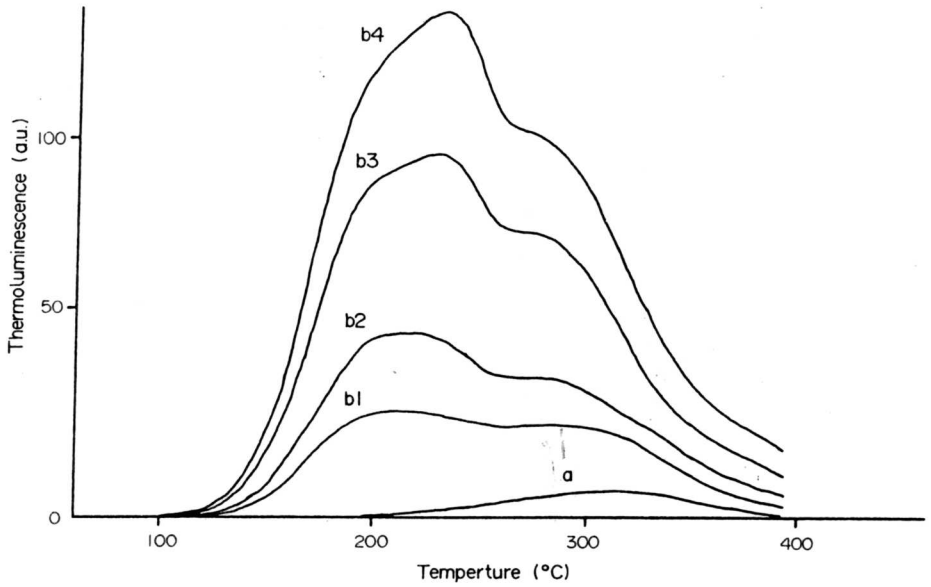

FIG. 4. TL spectra of C94 quartz sample. Blue filter BG12 Leitz. Heating rate; 5°C s^{-1}. Flowing nitrogen. The blackbody background was subtracted and the curves are averaged over ten of them. a: NTL; b: natural + dose; b1: 146 Gy; b2: 274 Gy; b3: 554 Gy; b4: 821 Gy. Two peaks, around 180 and 220°C are present on artificially induced TL and not on NTL, because they are not stable at room temperature. The "pre-dose" peak, around 100–110°C, can also be observed on this sample when it is glowed immediately after irradiation. It cannot be seen here because the curves were recorded several weeks after irradiation.

the red TL growth (Fig. 5). The Al signal is higher than the Ti signal and seems to initiate a second rise above 800 Gy. This should be confirmed by further experiments at higher doses, because this behaviour is very rare in ESR.

The results presented below for C94 sample are similar, qualitatively, to those obtained on other quartz grains extracted from various origins tested in the Clermont laboratory.

Blue TL exhibits a supralinear growth curve at high added doses (at least 4 kGy), whatever the temperature on the glow curve. At low dose, roughly between NTL, around 70 and 820 Gy, it is almost linear. A saturating exponential-like growth curve is observed when preheating (345°C for 10 s) is used (Fig. 5), also followed by a supralinear growth at high doses. RTL exhibits a saturating exponential-like growth at low doses, which has a tendency to become linear at high doses. A second rise, as for BTL, was never observed with RTL, even at very high doses.

It is not intended here to thoroughly discuss the comparisons, because more experimental and theoretical work is needed. Only a few remarks will accompany these preliminary results. Table 1 shows the palaeodoses and ages obtained by ESR and TL methods on C94 samples.

Table 1. Palaeodoses and ages obtained by ESR and TL methods on C94 sample

	ESR		TL
	Al	Ti	Red peak
Palaedoses* (Gy)	96 ± 7	80 ± 7	70 ± 5
Ages (10^3 yr)	20 ± 2	17 ± 2	13.7 ± 1.6

*The paleodose was derived from an exponential fit for ESR and using a "second glow" growth curve for TL. This can explain the discrepancy between different results. Annual doses are not equal because the used grains sizes were not the same for TL and ESR.

Concerning ESR studies, a first analysis was done on the same sediment. This sample, called TL44 (Yokoyama *et al.*, 1985a), gave exactly the same palaeodose for the Al centre (96 ± 9 Gy), but a little bit higher for the Ti centre (91 ± 18 Gy). If we take into account the statistical error, we can conclude that the samples TL 44 and C94 which are extracted from the same sediment are reproducible. These results show a good reliability of the ESR dating method.

For the annual dose, the ^{238}U, ^{226}Ra, ^{222}Rn, ^{228}Ra and ^{40}K activities of the C94 sediments have been determined by gamma-ray spectrometry using a high purity germanium detector (GeHP). Cosmic and

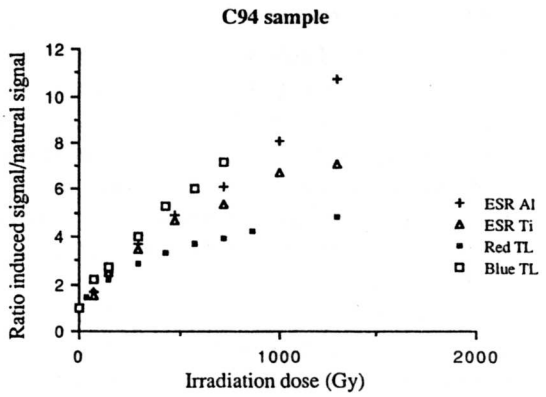

FIG. 5. Growth-curves for blue and red TL peaks and for Al and Ti centres of quartz C94. The curves are traced by the least-squares method.

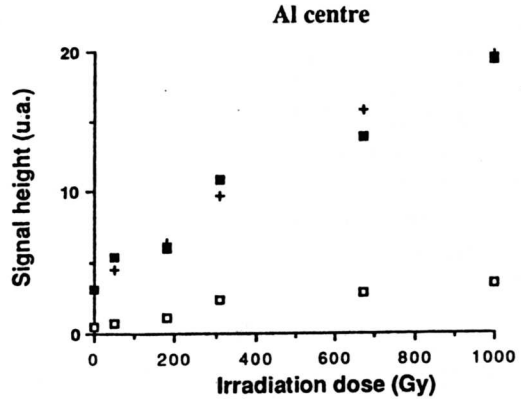

Fig. 6a

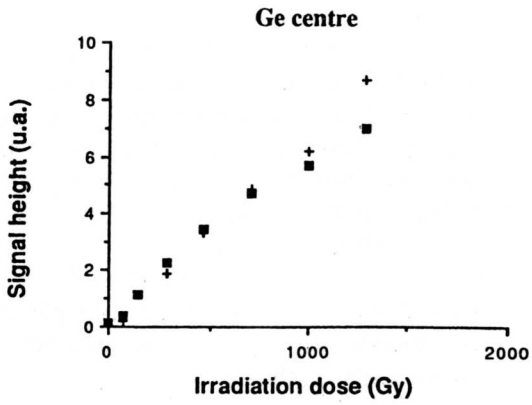

Fig. 6c

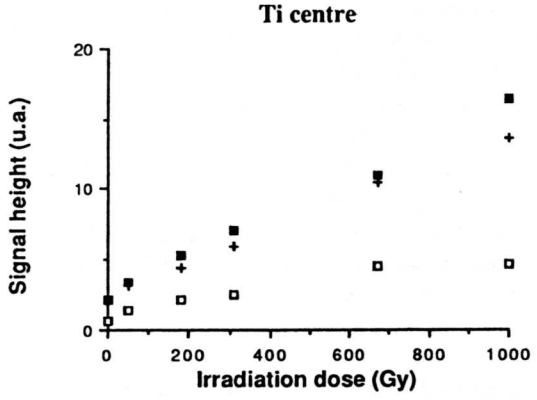

Fig. 6b

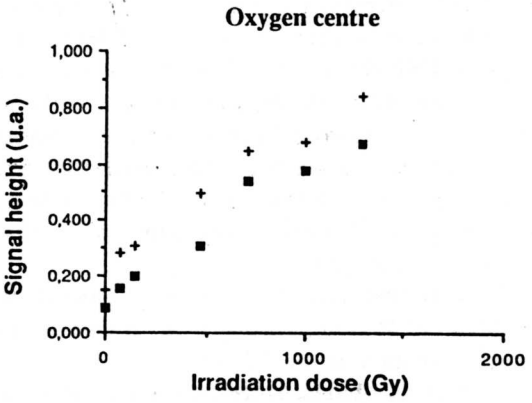

Fig. 6d

FIG. 6. Growth curves for Al, Ti, Ge and OH centres in C94 sample. For the four diagrams, crosses correspond to natural samples, black squares represent samples baked at 10°C and white squares show growth curves for samples annealed at 180°C.

internal alpha doses were calculated by Guérin (1983) for the TL44 sample. We used these results for C94 sample.

Recently, Bastin *et al.* (1990) found a tephra layer dated 10750 BP (^{14}C) in a core drilled out of peat-bogs in the south of the Chaîne des Puys, which they tentatively attributed to the Tartaret volcano (15–22 km north of the peat-bogs). Taking into account an age correction of ~1000–2000 yr for ^{14}C at this period (Stuiver *et al.*, 1986; Vogel, 1987), we could then get to about 11750–12750, which happens to fall within the error limits of the TL age (13700 ± 1600 yr).

The growth curves of the Al, Ti and Ge centres are compared (Fig. 6). The growth seems similar. But as we did not observe any Ge signal in the natural samples, it was impossible to use this centre to determine the C94 palaeodose. According to McKeever (1990), the Ge centre would correspond to the blue TL peak at 100°C which is not stable, and that can be seen only after recent irradiation. So we can deduce that the Ge centre does not correspond to the red TL peak. On the other hand, we can observe in an ESR sample that the Ge signal is not affected at 110°C. This contradiction between TL and ESR results is not explained yet. It seems that this question is complex and we do not have enough information to give more details for the moment.

Light effect

In order to test if sunlight had an effect on the signal height of quartz, two series of the same sample (C94) were prepared. One was exposed to daylight without any precaution before and during preparation. This one was called "light-exposed". The other was entirely protected from daylight ("light-obscured"). Figure 7 shows that there is no significant difference between "unexposed" and "exposed" samples for Al and Ti centres. These results are in agreement with TL measurements which indicate that

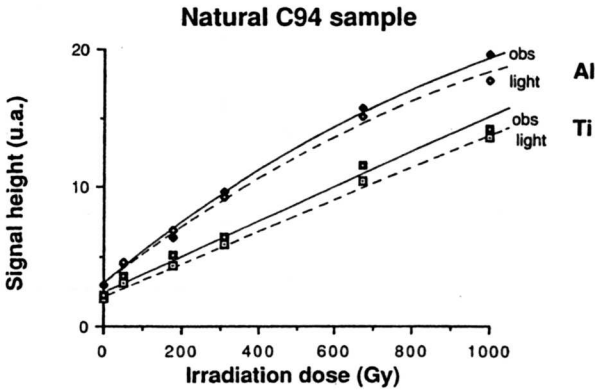

FIG. 7. Comparison between "obscurity" and "light" C94 natural samples for Al and Ti centres. obs = light-obscured and light = light-exposed.

the red TL peak is not sensitive to light exposure (Miallier *et al.*, 1990). The main blue peak decreases with light exposure. As several authors did before, we observed two components in the decay curve, corresponding to at least two components of the peak. The first decay is rapid (−30% after 1 min at 365 nm/226 Wm^{-2}) and then it becomes exponential (−50% after 100 min).

The pre-dose peak (100–110°C), not existing in natural TL, grows when the sample is lit, by a well-known phenomenon of phototransfer from deeper traps to shallower traps.

Thermal stability

The thermal experiments were not performed using the same furnace for TL (in the Clermont laboratory) and ESR (in the Paris laboratory), but the differences in behaviour are large enough not to be entirely due to temperature calibration of the furnaces.

Figure 8 shows that ESR signals disappear after an annealing temperature of 200°C while the signal height of TL peak is still about 65% of the natural sample's height.

The observed ESR centres' behaviour is similar to the behaviour observed in previous experiments (Yokoyama *et al.*, 1985b).

In C94 quartz, three peaks are detected by TL at 220, 320 and 380°C (Fig. 3). We heated our sample at 252, 352 and 406°C for 2 min in order to eliminate peak after peak. After each annealing, we observed our sample by ESR spectroscopy to see if there was an influence on the ESR signal height: after the 252°C annealing Al, Ti and Ge centres were destroyed.

This experiment reveals that the ESR centres do not have the same thermal stability as that of the red TL peak, and the main blue TL peak.

CONCLUSION

These experiments allow us to conclude that we did not find any correspondence between our observed ESR signals and TL peaks. Exception should be outlined for the 100–110°C peak, not studied in the present work, for which convincing correlations between TL and ESR were found (McKeever, 1990). The cause of the red TL peak in several natural quartz samples has been investigated from the point of view of impurity elements like europium and samarium content (Hashimoto *et al.*, 1986). These authors noticed a relationship between Eu content and ratios of red TL to total TL intensities.

From an ESR point of view, on a "very young" sample like C94, the sensitivity of the apparatus is important. Signals which can be observed by the TL method are not necessarily detectable by ESR spectroscopy, even more trap centres can be seen by this

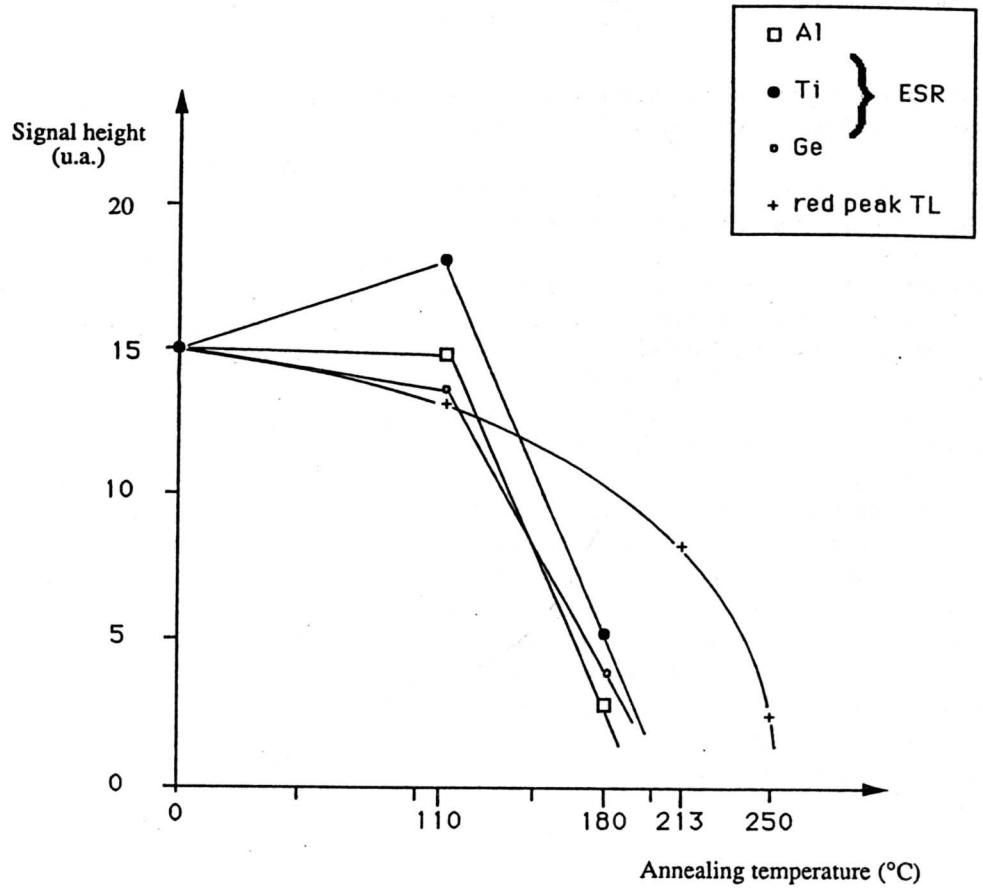

FIG. 8. Isochronal pulse annealing of the ESR centres and red TL peak. The samples have been heated during 16 h for each annealing temperature. This experiment was done with irradiated ESR samples (1288 Gy) and natural TL samples.

latter method. There is another possible explanation for why no correspondence between TL peaks and ESR signals was found. It may be that the TL donor corresponds to a double-electron trap which is not possible to detect by the ESR method.

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